

# PATENT ABSTRACTS OF JAPAN

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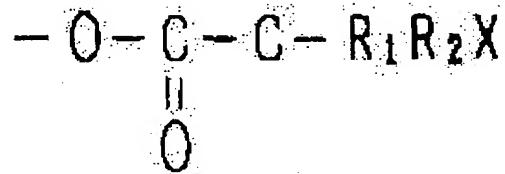
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## (54) RESIST COMPOSITION AND METHOD FOR FORMING MICROPATTERN

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a resist composition capable of enhancing contrast by incorporating a polymer to be allowed to increase its solubility in an alkaline developing solution by application of radiation and a contrast booster having a specified substituent in the molecule.

**SOLUTION:** The resist composition contains the polymer to be allowed to increase its solubility in the alkaline developing solution by application of radiation and the contrast booster having the substituent represented by the formula in which X is a halogen atom; and each of R<sub>1</sub> and R<sub>2</sub> is, independently, an H atom or an alkyl or phenyl group. This micropattern forming method comprises a process for coating the surface of a substrate with this resist composition to form a resist film; a process for selectively exposing the resist film, a process for heat treating it after the heat treatment, and a process for developing the resist film with the alkaline developing solution.



### LEGAL STATUS

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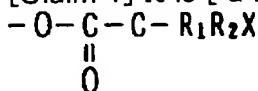
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## **CLAIMS**

[Claim(s)]

[Claim 1] It is [ a macromolecule polymer and ] a chemical formula [\*\* 1] in a molecule.



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、アルキル基、またはフェニル基であり、相互に同一でもよいし相違してもよい。)

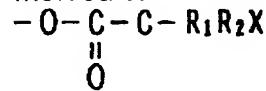
The resist constituent which has the contrast boost agent which comes out and has the substituent expressed.

[Claim 2] The resist constituent according to claim 1 with which said macromolecule polymer has the acidolysis nature machine to which the solubility over an alkali developer is made to increase in response to a side chain with an acid, and contains further the acid generator which produces an acid by the exposure of ionizing radiation.

[Claim 3] The resist constituent according to claim 1 or 2 with which said contrast boost agent is contained 0.5 to 20% of the weight to said giant-molecule polymer.

[Claim 4] The resist constituent according to claim 1 to 3 with which said contrast boost agent has at least one frame among a benzene frame, a cyclohexane frame, and an adamantane frame in the molecular structure.

[Claim 5] It is [ the macromolecule polymer which has the side chain to which react to with an acid and the solubility over an alkali developer is made to increase, the acid generator which produces an acid by the exposure of ionizing radiation, and ] a chemical formula [\*\* 2] in a molecule.



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、アルキル基、またはフェニル基であり、相互に同一でもよいし相違してもよい。)

The detailed pattern formation approach of having the process which applies the resist constituent which has the contrast boost agent which comes out and has the substituent expressed on the front face of a substrate, and forms the resist film, the 1st exposure process which exposes said resist film partially, the process which heat-treats said substrate after exposure, and the process which develops said exposed resist film with an alkali developer.

[Claim 6] The detailed pattern formation approach according to claim 5 that the time amount after said process which the 1st exposes, and to said process to heat-treat is less than 1 minute.

[Claim 7] The detailed pattern formation approach according to claim 5 or 6 of processing said substrate in the vacuum of  $1 \times 10^{-4}$  or less Torrs of pressures, nitrogen-gas-atmosphere mind,

or an argon ambient atmosphere till termination of said process to said process which the 1st exposes and to heat-treat.

[Claim 8] The detailed pattern formation approach including the process which forms further the thin film which becomes the bottom of said resist film, or a top from the poly aminoanisole sulfonic acid before said process which the 1st exposes according to claim 5 to 7.

[Claim 9] Furthermore, the detailed pattern formation approach including the 2nd exposure process which exposes the front face of said resist film by ultraviolet rays before a development process after said heat treatment process according to claim 5.

[Claim 10] The detailed pattern formation approach according to claim 9 exposed on the conditions which said contrast boost agent hydrolyzes by the part by the side of the front face of said resist film, and said contrast boost agent does not hydrolyze in other parts in said 2nd exposure process.

[Claim 11] The detailed pattern formation approach according to claim 9 or 10 that the absorption coefficient of said resist film in the wavelength region of the exposure light used at said 2nd exposure process is larger than it in the wavelength region of the exposure light used at said 1st exposure process.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the approach of forming a detailed pattern by the resist constituent and exposure, and development.

#### [0002]

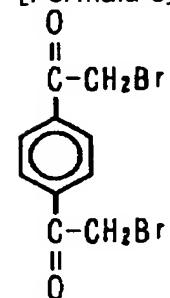
[Description of the Prior Art] Wiring width of face is made detailed with 0.18 micrometers, 0.15 micrometers, and 0.12 micrometers as the memory capacity of semiconductor memory increases with 1G bit, 4G bit, and 16G bit. Research of the chemistry magnification mold resist ingredient for forming such a detailed-sized pattern is progressing. In the pattern formation using a chemistry magnification mold resist ingredient, an acid is generated from the ingredient (acid generator) which generates an acid by the exposure of ionizing radiation (an electron ray, ultraviolet rays, an X-ray, focused ion beam, etc.), and it heat-treats after exposure. During heat treatment, this acid works as a catalyst and a macromolecule polymer becomes alkali fusibility. It can high-sensitivity-ize by the chain reaction using this acid catalyst. Moreover, a pattern without swelling can be formed by developing negatives in an alkali water solution.

#### [0003]

[Problem(s) to be Solved by the Invention] In the pattern formation using a chemistry magnification mold resist, in order to use the chain reaction of an acid catalyst, a reaction also attains to the part which is not exposed slightly. This is called diffusion of an acid and causes resolution degradation. Although resolution can be raised if chain reaction is controlled, sensibility falls. Although there is the approach of carrying out little addition of the alkali at a resist ingredient, and controlling diffusion of an acid, this approach is accompanied by sensibility fall in order to carry out deactivation of the acid.

[0004] The technique of preventing diffusion of an acid is proposed without adding a contrast boost agent into a resist ingredient, and following the fall of sensibility on it. A contrast boost agent is matter which changes with alkali from hydrophobicity to a hydrophilic property, and has the effectiveness which makes contrast of a resist pattern high. As an example of a contrast boost agent, it is [0005].

#### [Formula 3]



[0006] \*\*\*\*\*. If this contrast boost agent is added in a resist constituent and negatives are developed with an alkali developer, a bromine atom part will hydrolyze and the following

reaction will occur.

[0007]

[Formula 4]



[0008] By this reaction, a contrast boost agent becomes a hydrophilic property. If the part exposed among resist film dissolves in an alkali developer, the contrast boost agent contained in the part will become a hydrophilic property, and it will become easier to dissolve it in an alkali developer. The part which is not exposed among resist film is not dissolved in an alkali developer. For this reason, it is the contrast boost agent contained in this part in the hydrophobic state, and it is not dissolved in an alkali developer. That is, breadth and contrast become [ the difference of the solubility to the alkali developer of the exposed part and the part which is not exposed ] high.

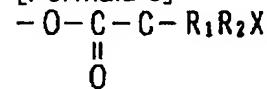
[0009] The purpose of this invention is offering the resist constituent which can raise contrast more.

[0010] Other purposes of this invention are offering the approach of forming a detailed pattern using the resist constituent which can raise contrast more.

[0011]

[Means for Solving the Problem] According to one viewpoint of this invention, it is [ the macromolecule polymer to which the solubility over an alkali developer is made to increase by the exposure of ionizing radiation, and ] a chemical formula [0012] in a molecule.

[Formula 5]



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、  
アルキル基、またはフェニル基であり、  
相互に同一でもよいし相違してもよい。)

[0013] The resist constituent which has the contrast boost agent which comes out and has the substituent expressed is offered.

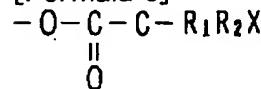
[0014] According to other viewpoints of this invention, the detailed pattern formation approach of having the process which applies the above-mentioned resist constituent on the front face of a substrate, and forms the resist film, the process which exposes said resist film partially, the process which heat-treats said substrate after exposure, and the process which develops said exposed resist film with an alkali developer is offered.

[0015] A contrast boost agent is hydrolyzed by existence of alkali in two steps, and the acid which has a carboxyl group is generated. Since this acid dissolves in alkali, it becomes easy to dissolve the part developed with the alkali developer in alkali increasingly.

[0016]

[Embodiment of the Invention] In the resist constituent by the 1st example of this invention, it is a chemical formula [0017] in a molecule.

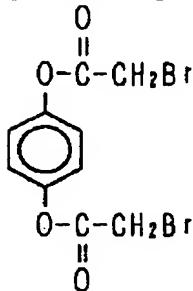
[Formula 6]



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、  
アルキル基、またはフェニル基であり、  
相互に同一でもよいし相違してもよい。)

[0018] The contrast boost agent which comes out and has the substituent expressed is added. As an example of a contrast boost agent, it is [0019].

[Formula 7]



[0020] \*\*\*\*\*.

[0021] By existence of an alkali water solution, two steps of the following hydrolysis reactions arise.

[0022]

[Formula 8]



[0023] Finally, the acid which has a carboxyl group is generated. For example, hydroxyacetic acid is generated when using the contrast boost agent expressed with a chemical formula 5. Since the matter finally generated is an acid, compared with the case where neutral alcohol is generated like a chemical formula 3, the solubility to an alkali water solution is high. For this reason, the contrast of a resist pattern can be raised more.

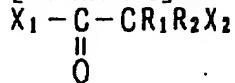
[0024] When various additions of a contrast boost agent were changed, the resist pattern was formed and the addition of the contrast boost agent to the giant-molecule polymer in a resist constituent was 0.5 – 20 % of the weight, it turned out that high contrast can be acquired.

[0025] When etching by using a resist pattern as a mask, it is necessary to secure sufficient etching resistance. Etching resistance can be raised by using the contrast boost agent which has a benzene frame, a cyclohexane frame, or an adamantane frame into the molecular structure.

[0026] Next, the example of the synthetic approach of an above-mentioned contrast boost agent is explained.

[0027] General formula [0028]

[Formula 9]



( $\text{X}_1$ 及び $\text{X}_2$ はハロゲン原子であり、相互に同一でもよいし相違してもよい。  
 $\text{R}_1$ 及び $\text{R}_2$ は水素原子、アルキル基、またはフェニル基であり、相互に同一でもよいし相違してもよい。)

[0029] It comes out and the matter A expressed and the matter B which has a hydroxyl group are dissolved into a solvent. A tetrahydrofuran can be used as a solvent. Let 10g and the amount of dissolutions of Matter A be the hydroxyl group and equimolecular amount of Matter B for the amount of dissolutions of Matter B to tetrahydrofuran 300cc Naka.

[0030] After dissolving Matter A and B in a solvent, it stirs in nitrogen-gas-atmosphere mind. Then, tetrahydrofuran 100cc in which the pyridine of Matter A and equimolar was dissolved is dropped over 1 hour. After dropping termination continues churning for 2 hours. The solution after churning is filtered and a solvent is distilled out of a filtrate. Thus, a contrast boost agent is separated by rinsing the matter of the shape of acquired powder.

[0031] The contrast boost agents 1-7 obtained are indicated to be the examples of combination of Matter A and B to drawing 1-7, respectively. The contrast boost agents 1-7 were added into the chemistry magnification mold resist ingredient, and the detailed pattern was formed. The result is shown in Table 1.

[0032]

[Table 1]

コントラ ストブー スト剤	1線使用			電子線使用		
	感度 mJ/cm <sup>2</sup>	コントラ スト	解像性	感度 μC/cm <sup>2</sup>	コントラ スト	解像性
1	22	9.2	◎	7	10.6	◎
2	19	10.5	◎	7	11.6	◎
3	20	11.2	◎	6	11.2	◎
4	20	10.5	◎	7	9.8	◎
6	19	11.9	◎	7	11.8	◎
7	25	10.5	◎	7	11.0	◎
なし	20	4.2	△	7	3.7	△
比較例1	21	6.2	○	8	5.5	○
比較例2	21	7.5	○	8	6.2	○

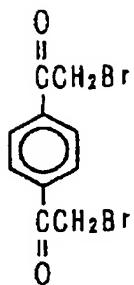
[0033] The used giant-molecule polymer is about 1:1 copolymer of PARAHIDOROKISHI styrene and TASHARU butyl acrylate, and is molecular weight about 10,000 thing. The used acid generator is triphenylsulfonium triflate. Contrast boost agent 0.05g was added to the resist basic constituent which consists of 1g of giant-molecule polymers, 0.05g of acid generators, and 5.5g of ethyl lactates, and the resist constituent for evaluation was compounded to it. As a developer, 2.38% of the weight of the tetramethylammonium water solution was used.

[0034] The resist film with a thickness of 0.6 micrometers was formed on the silicon substrate, and the PURIBE king for 2 minutes was performed at the temperature of 120 degrees C. After exposing, post baking for 2 minutes was performed at the temperature of 120 degrees C in the high vacuum ambient atmosphere of 3x10 to 5 or less Torrs of pressures. In addition, it is good also considering the temperature of post baking as 60-180 degrees C. Time amount from exposure to post baking was made into 40 or less seconds. In order to demonstrate enough the engine performance of a chemistry magnification mold resist ingredient, it is desirable to shorten time amount from exposure to post baking. According to the experiment of invention-in-this-application persons, it is desirable to make this time amount into 1 or less minute. Moreover, it is desirable to perform the process from exposure to post baking in the vacuum of 1x10 to 4 or less Torrs, nitrogen-gas-atmosphere mind, or an argon ambient atmosphere.

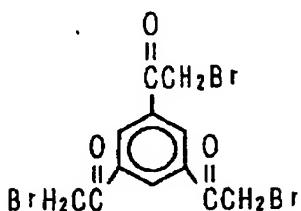
[0035] The contrast of Table 1 was searched for from the inclination of a sensitivity curve. Definition was evaluated by forming opening with a diameter of 0.2 micrometers in the resist film with a thickness of 0.6 micrometers. In addition, when electron beam lithography was performed, the antistatic film with a thickness of 0.02 micrometers it is thin from the poly aminoanisole sulfonic acid was formed on the front face of the resist film.

[0036] In addition, it is [0037] as the resist constituent which has not added the contrast boost agent for reference, and a contrast boost agent.

[Formula 10]

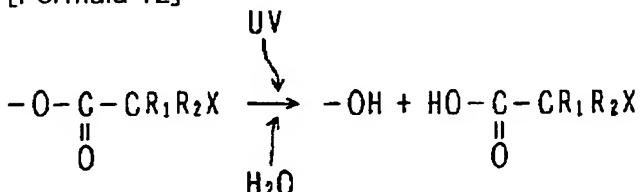


[0038] It is [0039] as the example 1 of a \*\*\*\*\* comparison, and a contrast boost agent.  
 [Formula 11]



[0040] Same evaluation was performed also with the example 2 of a \*\*\*\*\* comparison.  
 [0041] As shown in Table 1, the fall of the sensibility by having added the contrast boost agent was not seen. By adding the contrast boost agents 1-7 by the example, contrast is improving greatly irrespective of i line exposure and electron beam lithography. Moreover, high definition was able to be acquired reflecting improvement in contrast.  
 [0042] When the detailed pattern was formed using the resist ingredient of the positive type by the above-mentioned example, it turned out that the cross section of the resist pattern which remained after development may become T character-like. When it is neutralized by the alkali of the minute amount in air or the thing near the front face volatilizes among the acids in the resist film produced by exposure, since the acid concentration near the front face fell, this is considered. If the acid concentration near the front face falls, the chain reaction by the acid catalyst will become inadequate, and it will be hard coming to dissolve in a developer. For this reason, the surface layer of the resist film of a field which should dissolve remains in the shape of eaves, and the cross section of a resist pattern becomes T character-like.  
 [0043] If the cross section of a resist pattern becomes T character-like, it will become difficult to form a detailed pattern. Such a phenomenon becomes so remarkable that the contrast of a resist increases. Next, the formation approach of the detailed pattern by the 2nd example which can control the phenomenon in which a cross section becomes T character-like is explained.  
 [0044] In the 1st above-mentioned example, as shown in a chemical formula (8), the reaction by which the acid which a contrast boost agent hydrolyzes and has a carboxyl group by existence of an alkali developer is generated is used. Even if invention-in-this-application persons were the cases where an alkali solution did not exist, they discovered that the following reaction arose by irradiating ultraviolet rays at a contrast boost agent.

[0045]  
 [Formula 12]



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、  
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[0046] That is, if ultraviolet rays are irradiated at a contrast boost agent, the acid which is hydrolyzed by existence of the water in the resist film or atmospheric air, and has a carboxyl group will be generated. An increment of the content of the carboxylic acid in the resist film increases the solubility of the resist film to an alkali developer. It is predicted by exposing all the front faces of the resist film by ultraviolet rays, and raising the acidity near [ the ] the front face before development, that the solubility near the front face can be raised. In addition, it is not necessary to necessarily expose the whole front face of the resist film. What is necessary is just to expose, without distinguishing the part which should leave the resist film for the inside of the field where the detailed pattern which should be formed is arranged, and the part which should be removed.

[0047] When irradiating ultraviolet rays, it is desirable to make it the reaction of a chemical formula (12) occur only [ near the front face ]. For that purpose, it is desirable to use the ultraviolet rays of the big wavelength region of absorption by the resist film as ultraviolet rays which perform a complete exposure. For example, it is desirable to use the ultraviolet rays of the wavelength region which is easy to be absorbed rather than the ultraviolet rays or the electron ray for pattern formation.

[0048] If wavelength of the ultraviolet rays at the time of complete exposure is lengthened, ultraviolet rays will reach to the depths section of the resist film. Moreover, if wavelength is too short, the resist film will receive a damage according to the secondary operation by generating of ozone etc. In order to make the reaction of a chemical formula (12) start from the front face of the resist film in a field with a depth of 0.05 micrometers or less, it is desirable to use ultraviolet rays with a wavelength of 100nm – 500nm, and, specifically, it is more desirable to use the ultraviolet rays which are the wavelength of 150nm – 300nm.

[0049] It is desirable to perform complete exposure after postbake. By postbake, since the chain reaction by the acid catalyst is completed, complete exposure can be chemically performed in the stable condition.

[0050] The evaluation result at the time of performing complete exposure after postbake and forming a detailed pattern hereafter, is explained. The used resist ingredient is the same as that of what was used in the 1st above-mentioned example. As a contrast boost agent, the contrast boost agents 1–6 shown in drawing 1 – drawing 6 were used.

[0051] The diameter of opening which should form 0.6 micrometers of thickness of the resist film was set to 0.2 micrometers. Both prebaking and postbake were performed on the temperature of 110 degrees C, and the conditions for time amount 2 minutes. The ultraviolet rays used for complete exposure are the things of the wavelength of 254nm, and energy-density 5 mJ/cm<sup>2</sup>. The evaluation result of the definition of a resist pattern is shown in Table 2. It evaluated about the case where the case where i line is used as an exposure light for patterning, and an electron ray are used. In addition, the definition at the time of not performing complete exposure for a comparison is shown.

[0052]

[Table 2]

コントラスト ブースト剤		全面露光あり	全面露光なし
1	i線	○	◎
	電子線	○	◎
2	i線	○	◎
	電子線	○	◎
3	i線	△	○
	電子線	○	◎
4	i線	○	○
	電子線	○	◎
5	i線	△	◎
	電子線	○	◎
6	i線	○	◎
	電子線	○	◎

[0053] Notation O in Table 2 shows the case where the side attachment wall of opening becomes perpendicular to a substrate side mostly, and when the upper part of opening compares notation O caudad and it is a little thin, notation \*\* shows the case where the upper part of opening is thinner compared with the thing of notation O. As shown in Table 2, compared with the case where complete exposure is not performed, opening of a more desirable configuration can be formed by performing complete exposure before development.

[0054] Next, the 3rd example is explained. Although the 2nd example of the above explained the case where the resist ingredient of a positive type was used, the resist ingredient of a negative mold is used in the 3rd example. If the acidity near the resist film front face becomes weak in using the resist ingredient of a negative mold, the chain crosslinking reaction by the acid catalyst will become inadequate, and will become that negatives are easier to be developed. For this reason, the part of the shoulder of the resist pattern which remained by development dissolves in a developer, and a top face is roundish. If ultraviolet rays are irradiated completely and the acidity near the front face is raised before development, it will become is easy to be developed near the front face of the resist film. By removing the part of fixed thickness with a developer from the top face of the resist film which should remain, the cross-section configuration of a resist pattern can be brought close to a rectangle.

[0055] In addition, in order not to perform postbake after complete exposure, depending on the acid generated by complete exposure, chain crosslinking reaction does not arise in the resist film. In the field which is not exposed at the time of the exposure for patterning, since crosslinking reaction has not arisen, even if it exposes completely before development, it is possible to develop the part which should be developed.

[0056] The evaluation result of the effectiveness of complete exposure at the time of using the resist ingredient of a negative mold for below is explained. The used giant-molecule polymer is a PARAHIDOROKISHI styrene polymer, and is molecular weight about 10,000 thing. The methylation methylol melamine was used as a cross linking agent, and triphenylsulfonium triflate was used as an acid generator. Contrast boost agent 0.05g was added to the resist basic constituent which consists of 1g of giant-molecule polymers, 0.2g of cross linking agents, 0.05g of acid generators, and 5.5g of ethyl lactates, and the resist constituent for evaluation was compounded to it. The conditions of exposure and development are the same as that of the case of the 2nd example which used the positive resist. An evaluation result is shown in Table 3.

[0057]

[Table 3]

コントラスト ブースト剤		全面露光あり	全面露光なし
1	i線	○	◎
	電子線	○	◎
2	i線	△	◎
	電子線	○	◎
3	i線	△	○
	電子線	○	◎
4	i線	○	◎
	電子線	○	◎
5	i線	○	◎
	電子線	○	◎
6	i線	○	○
	電子線	○	◎

[0058] The semantics of notation [ in Table 3 ] O, O, and \*\* is the same as the semantics of each notation of Table 2. As shown in Table 3, also in the case of negative resist, compared with the case where complete exposure is not performed, opening of a more desirable configuration can be formed by performing complete exposure before development.

[0059]

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the approach of forming a detailed pattern by the resist constituent and exposure, and development.

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PRIOR ART

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[Description of the Prior Art] Wiring width of face is made detailed with 0.18 micrometers, 0.15 micrometers, and 0.12 micrometers as the memory capacity of semiconductor memory increases with 1G bit, 4G bit, and 16G bit. Research of the chemistry magnification mold resist ingredient for forming such a detailed-sized pattern is progressing. In the pattern formation using a chemistry magnification mold resist ingredient, an acid is generated from the ingredient (acid generator) which generates an acid by the exposure of ionizing radiation (an electron ray, ultraviolet rays, an X-ray, focused ion beam, etc.), and it heat-treats after exposure. During heat treatment, this acid works as a catalyst and a macromolecule polymer becomes alkali fusibility. It can high-sensitivity-ize by the chain reaction using this acid catalyst. Moreover, a pattern without swelling can be formed by developing negatives in an alkali water solution.

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#### EFFECT OF THE INVENTION

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[Effect of the Invention] The contrast and definition of a resist constituent can be raised without being accompanied by sensibility fall according to this invention, as explained above. By using this resist constituent, it becomes possible to form a detailed pattern.

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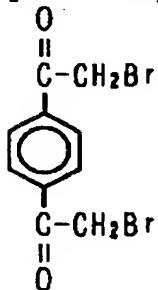
## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] In the pattern formation using a chemistry magnification mold resist, in order to use the chain reaction of an acid catalyst, a reaction also attains to the part which is not exposed slightly. This is called diffusion of an acid and causes resolution degradation. Although resolution can be raised if chain reaction is controlled, sensibility falls. Although there is the approach of carrying out little addition of the alkali at a resist ingredient, and controlling diffusion of an acid, this approach is accompanied by sensibility fall in order to carry out deactivation of the acid.

[0004] The technique of preventing diffusion of an acid is proposed without adding a contrast boost agent into a resist ingredient, and following the fall of sensibility on it. A contrast boost agent is matter which changes with alkali from hydrophobicity to a hydrophilic property, and has the effectiveness which makes contrast of a resist pattern high. As an example of a contrast boost agent, [0005]

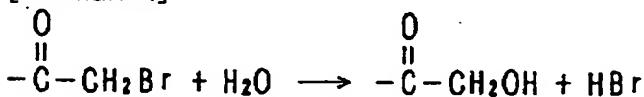
[Formula 3]



[0006] \*\*\*\*\*. If this contrast boost agent is added in a resist constituent and negatives are developed with an alkali developer, a bromine atom part will hydrolyze and the following reaction will occur.

[0007]

[Formula 4]



[0008] By this reaction, a contrast boost agent becomes a hydrophilic property. If the part exposed among resist film dissolves in an alkali developer, the contrast boost agent contained in the part will become a hydrophilic property, and it will become easier to dissolve it in an alkali developer. The part which is not exposed among resist film is not dissolved in an alkali developer. For this reason, it is the contrast boost agent contained in this part in the hydrophobic state, and it is not dissolved in an alkali developer. That is, breadth and contrast become [ the difference of the solubility to the alkali developer of the exposed part and the part which is not exposed ] high.

[0009] The purpose of this invention is offering the resist constituent which can raise contrast more.

[0010] Other purposes of this invention are offering the approach of forming a detailed pattern using the resist constituent which can raise contrast more.

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[Translation done.]

\* NOTICES \*

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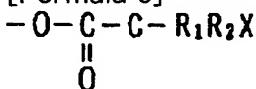
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MEANS

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[Means for Solving the Problem] According to one viewpoint of this invention, it is [ the macromolecule polymer to which the solubility over an alkali developer is made to increase by the exposure of ionizing radiation, and ] a chemical formula [0012] in a molecule.

[Formula 5]



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、アルキル基、またはフェニル基であり、相互に同一でもよいし相違してもよい。)

[0013] The resist constituent which has the contrast boost agent which comes out and has the substituent expressed is offered.

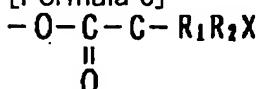
[0014] According to other viewpoints of this invention, the detailed pattern formation approach of having the process which applies the above-mentioned resist constituent on the front face of a substrate, and forms the resist film, the process which exposes said resist film partially, the process which heat-treats said substrate after exposure, and the process which develops said exposed resist film with an alkali developer is offered.

[0015] A contrast boost agent is hydrolyzed by existence of alkali in two steps, and the acid which has a carboxyl group is generated. Since this acid dissolves in alkali, it becomes easy to dissolve the part developed with the alkali developer in alkali increasingly.

[0016]

[Embodiment of the Invention] In the resist constituent by the 1st example of this invention, it is a chemical formula [0017] in a molecule.

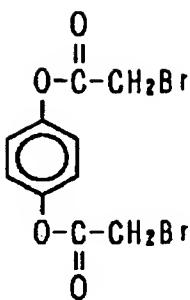
[Formula 6]



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、アルキル基、またはフェニル基であり、相互に同一でもよいし相違してもよい。)

[0018] The contrast boost agent which comes out and has the substituent expressed is added. As an example of a contrast boost agent, it is [0019].

[Formula 7]



[0020] \*\*\*\*\*.

[0021] By existence of an alkali water solution, two steps of the following hydrolysis reactions arise.

[0022]

[Formula 8]



[0023] Finally, the acid which has a carboxyl group is generated. For example, hydroxyacetic acid is generated when using the contrast boost agent expressed with a chemical formula 5. Since the matter finally generated is an acid, compared with the case where neutral alcohol is generated like a chemical formula 3, the solubility to an alkali water solution is high. For this reason, the contrast of a resist pattern can be raised more.

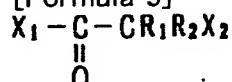
[0024] When various additions of a contrast boost agent were changed, the resist pattern was formed and the addition of the contrast boost agent to the giant-molecule polymer in a resist constituent was 0.5 – 20 % of the weight, it turned out that high contrast can be acquired.

[0025] When etching by using a resist pattern as a mask, it is necessary to secure sufficient etching resistance. Etching resistance can be raised by using the contrast boost agent which has a benzene frame, a cyclohexane frame, or an adamantane frame into the molecular structure.

[0026] Next, the example of the synthetic approach of an above-mentioned contrast boost agent is explained.

[0027] General formula [0028]

[Formula 9]



( $\text{X}_1$ 及び $\text{X}_2$ はハロゲン原子であり、相互に同一でもよいし相違してもよい。  
 $\text{R}_1$ 及び $\text{R}_2$ は水素原子、アルキル基、またはフェニル基であり、相互に同一でもよいし相違してもよい。)

[0029] It comes out and the matter A expressed and the matter B which has a hydroxyl group are dissolved into a solvent. A tetrahydrofuran can be used as a solvent. Let 10g and the amount of dissolutions of Matter A be the hydroxyl group and equimolecular amount of Matter B for the amount of dissolutions of Matter B to tetrahydrofuran 300cc Naka.

[0030] After dissolving Matter A and B in a solvent, it stirs in nitrogen-gas-atmosphere mind. Then, tetrahydrofuran 100cc in which the pyridine of Matter A and equimolar was dissolved is dropped over 1 hour. After dropping termination continues churning for 2 hours. The solution after churning is filtered and a solvent is distilled out of a filtrate. Thus, a contrast boost agent is separated by rinsing the matter of the shape of acquired powder.

[0031] The contrast boost agents 1-7 obtained are indicated to be the examples of combination of Matter A and B to drawing 1 – 7, respectively. The contrast boost agents 1-7 were added into the chemistry magnification mold resist ingredient, and the detailed pattern was formed. The

result is shown in Table 1.

[0032]

[Table 1]

コントラ ストブー スト剤	i 線使用			電子線使用		
	感度 mJ/cm <sup>2</sup>	コントラ スト	解像性	感度 μC/cm <sup>2</sup>	コントラ スト	解像性
1	22	9.2	◎	7	10.6	◎
2	19	10.5	◎	7	11.6	◎
3	20	11.2	◎	6	11.2	◎
4	20	10.5	◎	7	9.8	◎
6	19	11.9	◎	7	11.8	◎
7	25	10.5	◎	7	11.0	◎
なし	20	4.2	△	7	3.7	△
比較例1	21	6.2	○	8	5.5	○
比較例2	21	7.5	○	8	6.2	○

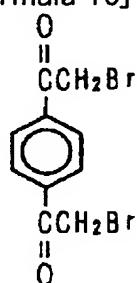
[0033] The used giant-molecule polymer is about 1:1 copolymer of PARAHIDOROKISHI styrene and TASHARU butyl acrylate, and is molecular weight about 10,000 thing. The used acid generator is triphenylsulfonium triflate. Contrast boost agent 0.05g was added to the resist basic constituent which consists of 1g of giant-molecule polymers, 0.05g of acid generators, and 5.5g of ethyl lactates, and the resist constituent for evaluation was compounded to it. As a developer, 2.38% of the weight of the tetramethylammonium water solution was used.

[0034] The resist film with a thickness of 0.6 micrometers was formed on the silicon substrate, and the PURIBE king for 2 minutes was performed at the temperature of 120 degrees C. After exposing, post baking for 2 minutes was performed at the temperature of 120 degrees C in the high vacuum ambient atmosphere of 3x10 to 5 or less Torrs of pressures. In addition, it is good also considering the temperature of post baking as 60-180 degrees C. Time amount from exposure to post baking was made into 40 or less seconds. In order to demonstrate enough the engine performance of a chemistry magnification mold resist ingredient, it is desirable to shorten time amount from exposure to post baking. According to the experiment of invention-in-this-application persons, it is desirable to make this time amount into 1 or less minute. Moreover, it is desirable to perform the process from exposure to post baking in the vacuum of 1x10 to 4 or less Torrs, nitrogen-gas-atmosphere mind, or an argon ambient atmosphere.

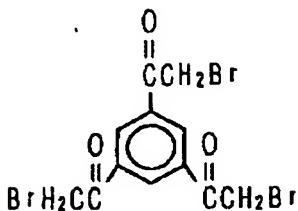
[0035] The contrast of Table 1 was searched for from the inclination of a sensitivity curve. Definition was evaluated by forming opening with a diameter of 0.2 micrometers in the resist film with a thickness of 0.6 micrometers. In addition, when electron beam lithography was performed, the antistatic film with a thickness of 0.02 micrometers it is thin from the poly aminoanisole sulfonic acid was formed on the front face of the resist film.

[0036] In addition, it is [0037] as the resist constituent which has not added the contrast boost agent for reference, and a contrast boost agent.

[Formula 10]



[0038] It is [0039] as the example 1 of a \*\*\*\*\* comparison, and a contrast boost agent.  
[Formula 11]



[0040] Same evaluation was performed also with the example 2 of a \*\*\*\*\* comparison.

[0041] As shown in Table 1, the fall of the sensibility by having added the contrast boost agent was not seen. By adding the contrast boost agents 1-7 by the example, contrast is improving greatly irrespective of i line exposure and electron beam lithography. Moreover, high definition was able to be acquired reflecting improvement in contrast.

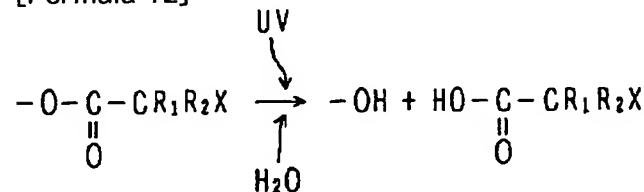
[0042] When the detailed pattern was formed using the resist ingredient of the positive type by the above-mentioned example, it turned out that the cross section of the resist pattern which remained after development may become T character-like. When it is neutralized by the alkali of the minute amount in air or the thing near the front face volatilizes among the acids in the resist film produced by exposure, since the acid concentration near the front face fell, this is considered. If the acid concentration near the front face falls, the chain reaction by the acid catalyst will become inadequate, and it will be hard coming to dissolve in a developer. For this reason, the surface layer of the resist film of a field which should dissolve remains in the shape of eaves, and the cross section of a resist pattern becomes T character-like.

[0043] If the cross section of a resist pattern becomes T character-like, it will become difficult to form a detailed pattern. Such a phenomenon becomes so remarkable that the contrast of a resist increases. Next, the formation approach of the detailed pattern by the 2nd example which can control the phenomenon in which a cross section becomes T character-like is explained.

[0044] In the 1st above-mentioned example, as shown in a chemical formula (8), the reaction by which the acid which a contrast boost agent hydrolyzes and has a carboxyl group by existence of an alkali developer is generated is used. Even if invention-in-this-application persons were the cases where an alkali solution did not exist, they discovered that the following reaction arose by irradiating ultraviolet rays at a contrast boost agent.

[0045]

[Formula 12]



(Xはハロゲン原子、R<sub>1</sub>及びR<sub>2</sub>は水素原子、  
アルキル基、またはフェニル基であり、  
相互に同一でもよいし相違してもよい。)

[0046] That is, if ultraviolet rays are irradiated at a contrast boost agent, the acid which is hydrolyzed by existence of the water in the resist film or atmospheric air, and has a carboxyl group will be generated. An increment of the content of the carboxylic acid in the resist film increases the solubility of the resist film to an alkali developer. It is predicted by exposing all the front faces of the resist film by ultraviolet rays, and raising the acidity near [ the ] the front face before development, that the solubility near the front face can be raised. In addition, it is not necessary to necessarily expose the whole front face of the resist film. What is necessary is just to expose, without distinguishing the part which should leave the resist film for the inside of the

field where the detailed pattern which should be formed is arranged, and the part which should be removed.

[0047] When irradiating ultraviolet rays, it is desirable to make it the reaction of a chemical formula (12) occur only [ near the front face ]. For that purpose, it is desirable to use the ultraviolet rays of the big wavelength region of absorption by the resist film as ultraviolet rays which perform a complete exposure. For example, it is desirable to use the ultraviolet rays of the wavelength region which is easy to be absorbed rather than the ultraviolet rays or the electron ray for pattern formation.

[0048] If wavelength of the ultraviolet rays at the time of complete exposure is lengthened, ultraviolet rays will reach to the depths section of the resist film. Moreover, if wavelength is too short, the resist film will receive a damage according to the secondary operation by generating of ozone etc. In order to make the reaction of a chemical formula (12) start from the front face of the resist film in a field with a depth of 0.05 micrometers or less, it is desirable to use ultraviolet rays with a wavelength of 100nm - 500nm, and, specifically, it is more desirable to use the ultraviolet rays which are the wavelength of 150nm - 300nm.

[0049] It is desirable to perform complete exposure after postbake. By postbake, since the chain reaction by the acid catalyst is completed, complete exposure can be chemically performed in the stable condition.

[0050] The evaluation result at the time of performing complete exposure after postbake and forming a detailed pattern hereafter, is explained. The used resist ingredient is the same as that of what was used in the 1st above-mentioned example. As a contrast boost agent, the contrast boost agents 1-6 shown in drawing 1 - drawing 6 were used.

[0051] The diameter of opening which should form 0.6 micrometers of thickness of the resist film was set to 0.2 micrometers. Both prebaking and postbake were performed on the temperature of 110 degrees C, and the conditions for time amount 2 minutes. The ultraviolet rays used for complete exposure are the things of the wavelength of 254nm, and energy-density 5 mJ/cm<sup>2</sup>. The evaluation result of the definition of a resist pattern is shown in Table 2. It evaluated about the case where the case where i line is used as an exposure light for patterning, and an electron ray are used. In addition, the definition at the time of not performing complete exposure for a comparison is shown.

[0052]

[Table 2]

コントラスト ブースト剤		全面露光あり	全面露光なし
1	i 線	○	◎
	電子線	○	◎
2	i 線	○	◎
	電子線	○	◎
3	i 線	△	○
	電子線	○	◎
4	i 線	○	○
	電子線	○	◎
5	i 線	△	◎
	電子線	○	◎
6	i 線	○	◎
	電子線	○	◎

[0053] Notation O in Table 2 shows the case where the side attachment wall of opening becomes perpendicular to a substrate side mostly, and when the upper part of opening compares notation O caudad and it is a little thin, notation \*\* shows the case where the upper part of opening is thinner compared with the thing of notation O. As shown in Table 2, compared with the case where complete exposure is not performed, opening of a more desirable configuration can be formed by performing complete exposure before development.

[0054] Next, the 3rd example is explained. Although the 2nd example of the above explained the case where the resist ingredient of a positive type was used, the resist ingredient of a negative mold is used in the 3rd example. If the acidity near the resist film front face becomes weak in using the resist ingredient of a negative mold, the chain crosslinking reaction by the acid catalyst will become inadequate, and will become that negatives are easier to be developed. For this reason, the part of the shoulder of the resist pattern which remained by development dissolves in a developer, and a top face is roundish. If ultraviolet rays are irradiated completely and the acidity near the front face is raised before development, it will become is easy to be developed near the front face of the resist film. By removing the part of fixed thickness with a developer from the top face of the resist film which should remain, the cross-section configuration of a resist pattern can be brought close to a rectangle.

[0055] In addition, in order not to perform postbake after complete exposure, depending on the acid generated by complete exposure, chain crosslinking reaction does not arise in the resist film. In the field which is not exposed at the time of the exposure for patterning, since crosslinking reaction has not arisen, even if it exposes completely before development, it is possible to develop the part which should be developed.

[0056] The evaluation result of the effectiveness of complete exposure at the time of using the resist ingredient of a negative mold for below is explained. The used giant-molecule polymer is a PARAHIDOROKISHI styrene polymer, and is molecular weight about 10,000 thing. The methylation methylol melamine was used as a cross linking agent, and triphenylsulfonium triflate was used as an acid generator. Contrast boost agent 0.05g was added to the resist basic constituent which consists of 1g of giant-molecule polymers, 0.2g of cross linking agents, 0.05g of acid generators, and 5.5g of ethyl lactates, and the resist constituent for evaluation was compounded to it. The conditions of exposure and development are the same as that of the case of the 2nd example which used the positive resist. An evaluation result is shown in Table 3.

[0057]

[Table 3]

コントラスト ブースト剤		全面露光あり	全面露光なし
1	i線	○	◎
	電子線	○	◎
2	i線	△	◎
	電子線	○	◎
3	i線	△	○
	電子線	○	◎
4	i線	○	◎
	電子線	○	◎
5	i線	○	◎
	電子線	○	◎
6	i線	○	○
	電子線	○	◎

[0058] The semantics of notation [ in Table 3 ] O, O, and \*\* is the same as the semantics of each notation of Table 2. As shown in Table 3, also in the case of negative resist, compared with the case where complete exposure is not performed, opening of a more desirable configuration can be formed by performing complete exposure before development.

[0059] Probably, there is effectiveness of complete exposure, also when using other giant-molecule polymers, although the 2nd and 3rd examples of the above explained the case where a PARAHIDOROKISHI styrene-TASHARU butyl acrylate copolymer and a PARAHIDOROKISHI styrene polymer were used as a giant-molecule polymer, respectively.

[0060] Although this invention was explained in accordance with the example above, this invention is not restricted to these. For example, probably, it will be obvious to this contractor for various modification, amelioration, combination, etc. to be possible.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the reaction which compounds the contrast boost agent 1 by the example of this invention.

[Drawing 2] It is drawing showing the reaction which compounds the contrast boost agent 2 by the example of this invention.

[Drawing 3] It is drawing showing the reaction which compounds the contrast boost agent 3 by the example of this invention.

[Drawing 4] It is drawing showing the reaction which compounds the contrast boost agent 4 by the example of this invention.

[Drawing 5] It is drawing showing the reaction which compounds the contrast boost agent 5 by the example of this invention.

[Drawing 6] It is drawing showing the reaction which compounds the contrast boost agent 6 by the example of this invention.

[Drawing 7] It is drawing showing the reaction which compounds the contrast boost agent 7 by the example of this invention.

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[Translation done.]

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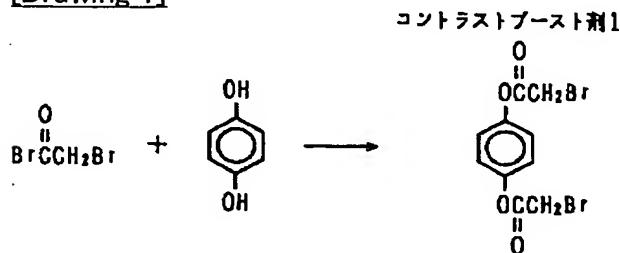
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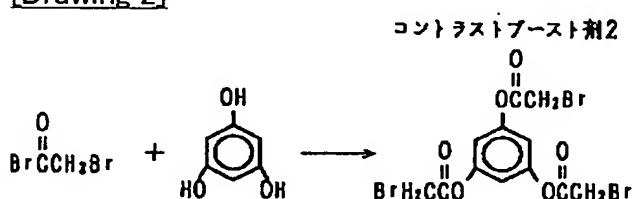
DRAWINGS

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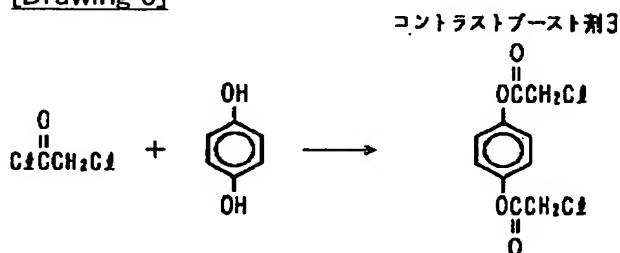
[Drawing 1]



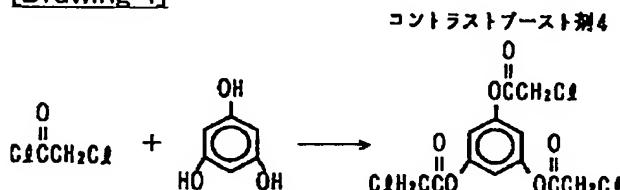
[Drawing 2]



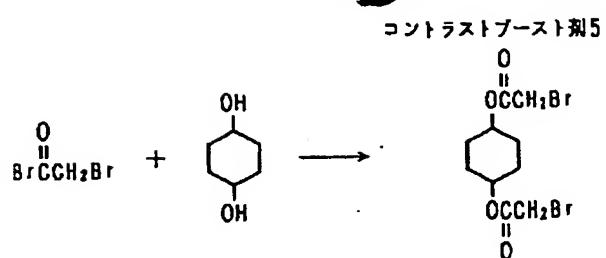
[Drawing 3]



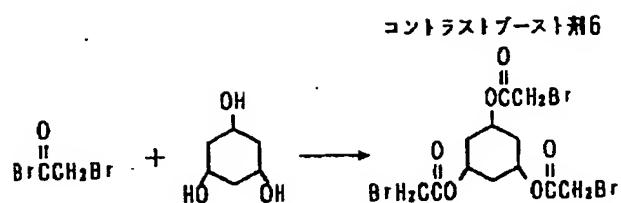
[Drawing 4]



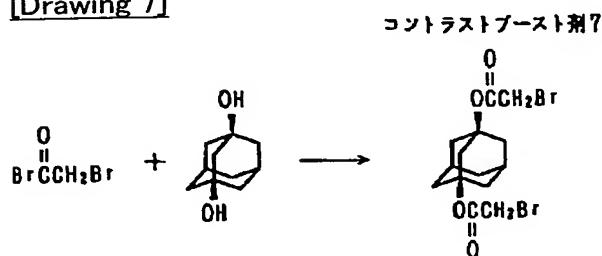
[Drawing 5]



[Drawing 6]



[Drawing 7]




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[Translation done.]